

## Geometrical Structures of the First Solvation Shell of the $[\text{PdCl}_4]^{2-}$ Core: Charge-Dipole vs Dipole-Dipole Interaction of $(\text{Pd}^{\text{II}} \cdots \text{Solvent})$

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Since the weak vertical interactions of  $(\text{Pt} \cdots \text{H}_2\text{O})$  in square planar Pt complexes were theoretically suggested by Kozelka *et al.*, axial metal-solvent interactions in square planar  $d^8$ -metal complexes have been the focus of various theoretical and experimental approaches focused on both geometrical structure and catalytic activity on reactions.<sup>1-4</sup> The weak  $(\text{M} \cdots \text{L})$  interaction for the solvation is formed from the various interactive components like the charge-dipole, dipole-dipole, and hydrogen bond interactions. From the results of Kozelka *et al.*,<sup>1</sup> the square pyramidal structures of Pt complexes with vertical  $(\text{Pt} \cdots \text{HO}, \text{Pt} \cdots \text{OH})$  interactions are optimized. The binding energies of  $(\text{OH} \cdots \text{Pt})$  and  $(\text{HO} \cdots \text{Pt})$  are about 11 and 4 kcal/mol, respectively. The distance of the apical  $(\text{Pt} \cdots \text{O})$  interaction is about 3.3-3.5 Å. From the calculations of the Deeth group,<sup>2</sup> we know the square pyramidal structures with vertical  $(\text{M} \cdots \text{OH}_2)$  interactions, as optimized at the LDA level. The binding energy of  $(\text{M} \cdots \text{OH}_2)$  is about 5 kJ/mol, and the  $(\text{M} \cdots \text{OH}_2)$  distance is about 2.6-2.8 Å. The five-coordinate structure of the GC calculation was not optimized.

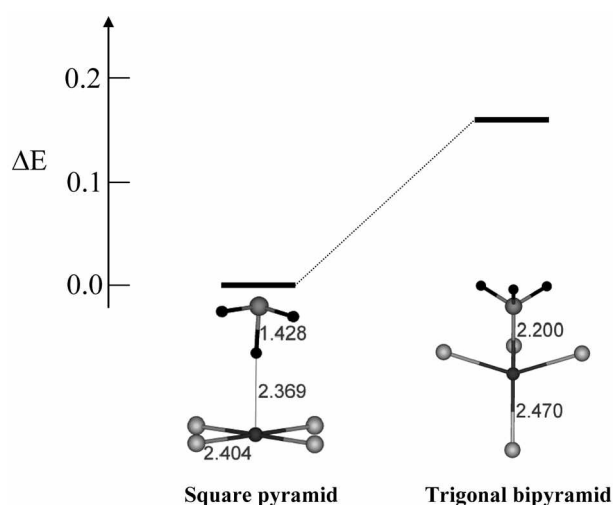
From the experimental results of Bröring and Brandt,<sup>3</sup> stable square-pyramidal or trigonal-bipyramidal  $\text{Pd}^{\text{II}}$  complexes with axial chemical  $(\text{Pd}-\text{L})$  bonds both in solution and the solid state were observed. The geometrical structures depend on the amount of phosphane ligand. In the water solution state,  $[\text{PdCl}_4]^{2-}(\text{H}_2\text{O})_2$  with two  $(\text{M} \cdots \text{OH}_2)$  interactions in the apical position of  $\text{PdCl}_4^{2-}$  was experimentally observed by Caminiti *et al.*<sup>4</sup> The geometrical structure of  $[\text{PdCl}_4]^{2-}(\text{H}_2\text{O})_2$  with two  $\text{H}_2\text{O}$  molecules coordinating has distorted octahedral symmetry.

For the ligand exchange reactions associated with the vertical  $(\text{Pd}^{\text{II}} \cdots \text{solvent})$  interaction, the reaction mechanisms are found to be proceeded via a vertically five-coordinated transition state  $([\text{PdL}_5]^\ddagger)$  leading to trigonal bipyramidal geometry.<sup>5-7</sup> In the ligand exchange of  $\{\text{Pd}(\text{PH}_3)_2\text{Cl}_2 + \text{H}_2\text{O}\}$  investigated by Park *et al.*,<sup>8,9</sup> the pentacoordinated Pd complex at the transition state has a square pyramidal geometry. The  $d_{z^2}$ -orbital of  $\text{Pd}^{\text{II}}$  interacts with the lone pair orbital of the fifth  $\text{H}_2\text{O}$  ligand at the vertical position and the four ligands simultaneously interact with a  $d_{x^2-y^2}$ -orbital in the mean plane. By the results of Lin and Hall,<sup>10</sup> the ligand dissociation process of Pd complexes was explained *via* square pyramidal and trigonal bipyramidal structures.

Although the geometrical structures of the first solvation shell of the  $\text{Pd}(\text{II})$  complexes have already been studied by some groups, further investigations would seem to be worthwhile on the basis of the following points. (i) In the first solvation shell of square planar  $d^8$ -metal complexes, the geometrical structures of the vertical  $(\text{M} \cdots \text{S})$  interactions were optimized by Kozelka *et al.* But some groups were not optimized. Does the vertical interaction in the first solvation shell exist or not? (ii) The  $(\text{M} \cdots \text{S})$  and  $(\text{L} \cdots \text{S})$  interactions for the solvation are formed from the various interactive components. Which type interactions are more stable? (iii) The interaction between the  $d^8$ -metal and solvents are formed with the coordination of the N- and O-atoms (hard  $\sigma$ -donor properties) and the P-atom (soft  $\sigma$ -donor and  $\pi$ -acceptor properties) on the solvent. Are the intensity of the axial interactions between Pd and the N-, O-, and P-atom on the ligand strong or weak? To answer these questions, we optimized the geometrical structures of the first solvation shell of the  $[\text{PdCl}_4]^{2-}$  core formed by the weak  $(\text{M} \cdots \text{S})$  interaction between the complex and solvent.

To get relatively stable structure between square pyramid and trigonal bipyramid, the structure and vibrational frequency of pentacoordinated Pd complex dianions with the MP2 method were optimized and analyzed, respectively. Based on the optimized square pyramidal structure, the equilibrium geometrical structures of  $\{[\text{PdCl}_4]^{2-} \cdot n\text{PH}_3, (n = 1-5)\}$ ,  $\{[\text{PdCl}_4]^{2-} \cdot n\text{NH}_3, (n = 1-5)\}$ , and  $\{[\text{PdCl}_4]^{2-} \cdot n\text{H}_2\text{O}, (n = 1-5)\}$  were fully optimized with the B3P86 method. All the calculations were performed with the 6-311+G\*\* (LanL2DZ + f-function for Pd;  $\alpha = 1.472^{11}$ ) basis set using Gaussian 03.<sup>12</sup> The hybrid B3P86 density functional utilizes the exchange function of Becke<sup>13</sup> in conjunction with the Perdew 1986 correlation function.<sup>14</sup> In addition, the atomic charges of the natural bond orbital (NBO)<sup>15</sup> of the Pd complexes were analyzed.

To investigate relatively stable geometry of pentacoordinated  $\text{Pd}^{\text{II}}$  complex dianion with the vertical  $(\text{Pd} \cdots \text{PH}_3)$  interaction, the structures and relative energies of square pyramidal and trigonal bipyramidal types were represented in Figure 1. The square pyramidal geometry of  $\{[\text{PdCl}_4]^{2-} \cdot \text{PH}_3\}$  (**outer sphere complex**) is more stable than trigonal bipyramidal type of  $[\text{PdCl}_4(\text{PH}_3)]^{2-}$  (**inner sphere complex**). The relative energy of trigonal bipyramid with respect to square



**Figure 1.** Relative energies (eV) between optimized square pyramidal and trigonal bipyramidal types of the pentacoordinate Pd complex dianions at the MP2/6-311+G\*\* (LanL2DZ + f-function for Pd;  $\alpha = 1.472$ ) level. (● : H, ● : P, ○ : Cl, ● : Pd).

pyramid is 0.18 eV. Our results are in good agreement with the experimental results,<sup>3</sup> which depend on the amount of phosphane ligand.

After the examination of the relative stability between two types, we optimized the geometrical structures of  $\{[\text{PdCl}_4]^{2-} \cdot n\text{PH}_3, (n = 1-5)\}$ ,  $\{[\text{PdCl}_4]^{2-} \cdot n\text{NH}_3, (n = 1-5)\}$ , and  $\{[\text{PdCl}_4]^{2-} \cdot n\text{H}_2\text{O}, (n = 1-5)\}$ , and they are drawn in Figure 2, including the distances and HOMOs. In the solvated Pd-complexes, a square  $[\text{PdCl}_4]^{2-}$  plane is located at a core part of the first solvation shell. In the solvated tetramer and pentamer, the first solvation shell with  $\{[\text{PdCl}_4]^{2-} \cdots \text{solvent}\}$  is complete. The structures of solvations with direct (Pd  $\cdots$  H) and (Cl  $\cdots$  H) interactions in the upper direction are denoted as (A) and (B), respectively.  $[\text{PdCl}_4]^{2-} \cdot n\text{H}_2\text{O}$  with two (Cl  $\cdots$  H) interactions in the same direction is denoted as (C).

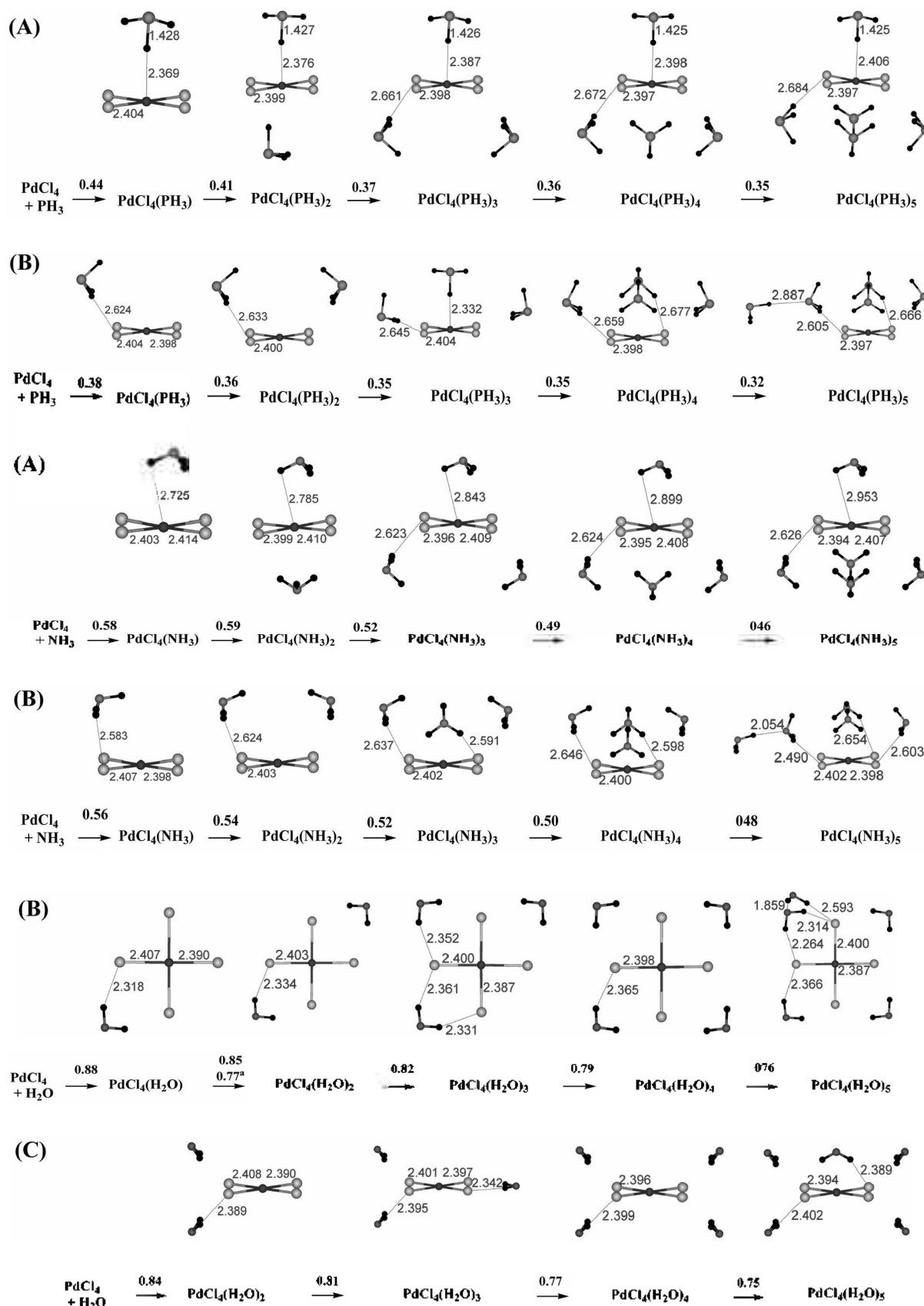
In the (A) type of  $[\text{PdCl}_4]^{2-} \cdot n\text{PH}_3$ , a H atom of  $\text{PH}_3$  directly coordinates with a positively charged  $\text{Pd}^{\text{II}}$  dication in the vertical direction of the  $[\text{PdCl}_4]^{2-}$  core. In the solvated dimer, the  $\text{Pd}^{\text{II}}$  dication directly interacts with two phosphines in the axially "up and down" directions. In (A) of  $[\text{PdCl}_4]^{2-} \cdot n\text{PH}_3$ , the vertical (Pd  $\cdots$  HPH<sub>2</sub>) interaction is formed with a charge-dipole interaction between  $\text{Pd}^{\text{II}}$  and  $\text{PH}_3$ . In the HOMO, the probability density between  $\text{Pd}^{\text{II}}$  and HPH<sub>2</sub> has appeared. From the trimer to pentamer, the other phosphines, except for a vertical  $\text{PH}_3$  molecule, are symmetrically located at the lower inclined plane of  $[\text{PdCl}_4]^{2-}$ . That is, two H atoms of  $\text{PH}_3$  mainly interact with two chlorines of  $[\text{PdCl}_4]^{2-}$  through a hydrogen bond. Simultaneously, the  $\text{PH}_3$  solvent partially interacts with the occupied  $d_{z^2}$ -orbital through a dipole-dipole interaction. With increasing solvation size, the vertical  $R_{\text{Pd} \cdots \text{H}}$  and the bridging  $R_{\text{P} \cdots \text{H}}$  distances gradually increase and decrease, respectively. Also, the  $R_{\text{Cl} \cdots \text{H}}$  distance of the hydrogen-bond increases. Our optimized distances are in good agreement with the previous theoretical values ( $R_{\text{Pd} \cdots \text{H}} = 3.3-3.8 \text{ \AA}$ ,  $R_{\text{P} \cdots \text{H}} = 3.75 \text{ \AA}$ ).<sup>1,2</sup>

In (B) of  $[\text{PdCl}_4]^{2-} \cdot n\text{PH}_3$ , the phosphines are located on the upper inclined plane of  $[\text{PdCl}_4]^{2-}$ . Two H atoms of  $\text{PH}_3$  mainly interact with two Cl atoms of  $[\text{PdCl}_4]^{2-}$  via hydrogen bonds. Simultaneously, the  $\text{PH}_3$  solvent partially interacts with the occupied  $d_{z^2}$ -orbital via a dipole-dipole interaction. In the trimer, a H atom of the third  $\text{PH}_3$  strongly interacts with the  $\text{Pd}^{\text{II}}$  dication in the vertical position and the dipole-dipole interaction between the other  $\text{PH}_3$  solvent and the  $d_{z^2}$ -orbital is weakened. As a result, the first and second  $\text{PH}_3$  solvent molecules are in line with the square  $[\text{PdCl}_4]^{2-}$  plane. The distances ( $R_{\text{Pd} \cdots \text{H}}$ ,  $R_{\text{Cl} \cdots \text{H}}$ ) in the trimer of (B) are shorter than the corresponding distances in the (A) type. With increasing solvation size, the binding energies of  $\{[\text{PdCl}_4]^{2-} \cdot n\text{PH}_3, (n = 1-5)\}$  decrease stepwise. The binding energies of the (A) type are larger than the corresponding energies of the (B) type. In the pentamer of the (B) type, although the fifth  $\text{PH}_3$  at the second shell is bound to the fourth  $\text{PH}_3$  in the first shell, the decreasing gap of the binding energy is regular in fashion.

In the (A) type of  $[\text{PdCl}_4]^{2-} \cdot n\text{NH}_3$ , a positively charged  $\text{Pd}^{\text{II}}$  core mainly interacts with the polar N atom of  $\text{NH}_3$  in the vertical position via a charge-dipole interaction. Simultaneously, two H atoms of  $\text{NH}_3$  weakly interact with the two Cl atoms of  $[\text{PdCl}_4]^{2-}$  through a hydrogen bond. In the solvated dimer, the positive  $\text{Pd}^{\text{II}}$  dication directly interacts with two  $\text{NH}_3$  solvent molecules in the upper and lower positions of  $[\text{PdCl}_4]^{2-}$ . From the trimer to pentamer, the (A) types of  $[\text{PdCl}_4]^{2-} \cdot n\text{NH}_3$  are similar to the (A) types of  $[\text{PdCl}_4]^{2-} \cdot n\text{PH}_3$ . With increasing size, the vertical  $R_{\text{Pd} \cdots \text{H}}$  distance of the charge-dipole interaction and the  $R_{\text{Cl} \cdots \text{H}}$  distance of the hydrogen bond increases, while the  $R_{\text{P} \cdots \text{Cl}}$  distance in  $[\text{PdCl}_4]^{2-}$  decreases.

In (B) of  $[\text{PdCl}_4]^{2-} \cdot n\text{NH}_3$ , two H atoms of  $\text{NH}_3$  interact with two Cl atoms through hydrogen bonds on the upper side of  $[\text{PdCl}_4]^{2-}$  and simultaneously, the  $\text{NH}_3$  solvent interacts with the  $d_{z^2}$ -orbital through dipole-dipole interactions. In the HOMO, due to the dipole-dipole interaction between  $\text{NH}_3$  and the  $d_{z^2}$ -orbital, the probability density in the N atom of the two  $\text{NH}_3$  solvent molecules has appeared. Because of the charge-dipole, dipole-dipole, and hydrogen bond interactions between  $[\text{PdCl}_4]^{2-}$  and  $\text{NH}_3$ , the binding energies of  $\{[\text{PdCl}_4]^{2-} \cdot n\text{NH}_3, (n = 1-5)\}$  are relatively large. With increasing cluster size, the interaction between  $[\text{PdCl}_4]^{2-}$  and  $\text{NH}_3$  becomes weaker. The binding energies decrease stepwise. In the (A) type, the binding energy (0.59 eV) of the dimer with two (charge  $\cdots$  dipole) interactions is larger than that (0.58 eV) of the monomer.

In  $\{[\text{PdCl}_4]^{2-} \cdot n\text{H}_2\text{O}, (n = 1-5)\}$ , the geometrical structures with hydrogen bonds between the two Cl atoms and  $\text{H}_2\text{O}$  are optimized, while the structures with the vertical (Pd  $\cdots$  H<sub>2</sub>O) interaction are not optimized. To obtain vertically solvated  $\text{Pd}^{\text{II}}$  complexes, although a  $\text{H}_2\text{O}$  molecule is forced to approach the square  $[\text{PdCl}_4]^{2-}$  plane in the axial position, the  $\text{H}_2\text{O}$  molecule moves to the square plane of  $[\text{PdCl}_4]^{2-}$  to make the hydrogen bond. In the (C) type, two  $\text{H}_2\text{O}$  molecules interact with two Cl atoms in the upper and lower inclined plane of the same direction. From the dimer to



**Figure 2.** Optimized geometrical structures including the  $d_{z^2}$ -orbital (HOMO) and the binding energies (eV) of the phosphine  $\{[\text{PdCl}_4]^{2-} \cdot n\text{PH}_3, (n = 1-5)\}$ , ammonia  $\{[\text{PdCl}_4]^{2-} \cdot n\text{NH}_3, (n = 1-5)\}$  and water  $\{[\text{PdCl}_4]^{2-} \cdot n\text{H}_2\text{O}, (n = 1-5)\}$  solvation of the  $[\text{PdCl}_4]^{2-}$  core. The structures with  $(\text{Pd}^{\text{II}} \cdots \text{H})$  and  $(\text{Cl} \cdots \text{H})$  interactions are denoted as (A) and (B), respectively.  $\{[\text{PdCl}_4]^{2-} \cdot n\text{H}_2\text{O}, (n = 2-5)\}$  with two  $(\text{Cl} \cdots \text{H})$  interactions are denoted as (C). (●: H, ●: N, ●: O, ●: P, ○: Cl, ●: Pd). "Ref. 2.

**Table 1.** Average atomic charges (NBO, au) of the equilibrium structures of  $\{[\text{PdCl}_4]^{2-} \cdot n\text{PH}_3, (n = 1-5)\}$  and  $\{[\text{PdCl}_4]^{2-} \cdot n\text{NH}_3, (n = 1-5)\}$ 

compound	type	charge			
		$Q_{\text{Pd}}$	$Q_{\text{P}}$	$Q_{\text{H}}$	$Q_{\text{Cl}}$
$[\text{PdCl}_4]^{2-} \cdot \text{PH}_3$	(A)	0.963	0.047 <sup>a</sup>	0.187 <sup>c</sup>	-0.740
	(B)	1.040	0.037 <sup>b</sup>	0.078 <sup>d</sup>	-0.771
$[\text{PdCl}_4]^{2-} \cdot 2\text{PH}_3$	(A)	0.946	0.062 <sup>a</sup>	0.153 <sup>c</sup>	-0.744
	(B)	1.014	0.049 <sup>b</sup>	0.065 <sup>d</sup>	-0.772
$[\text{PdCl}_4]^{2-} \cdot 3\text{PH}_3$	(A)	0.935	0.073 <sup>a</sup>	0.138 <sup>c</sup>	-0.753
	(B)	0.982	0.061 <sup>b</sup>	0.054 <sup>d</sup>	-0.772
$[\text{PdCl}_4]^{2-} \cdot 4\text{PH}_3$	(A)	0.916	0.080 <sup>a</sup>	0.133 <sup>c</sup>	-0.755
	(B)	0.974	0.073 <sup>b</sup>	0.040 <sup>d</sup>	-0.773
$[\text{PdCl}_4]^{2-} \cdot 5\text{PH}_3$	(A)	0.910	0.088 <sup>a</sup>	0.110 <sup>c</sup>	-0.758
	(B)	0.966	0.081 <sup>b</sup>	0.039 <sup>d</sup>	-0.773
		$Q_{\text{Pd}}$	$Q_{\text{N}}$	$Q_{\text{H}}$	$Q_{\text{Cl}}$
$[\text{PdCl}_4]^{2-} \cdot \text{NH}_3$	(A)	1.040	-0.581 <sup>a</sup>	0.190 <sup>c</sup>	-0.751
	(B)	1.053	-0.604 <sup>b</sup>	0.146 <sup>d</sup>	-0.762
$[\text{PdCl}_4]^{2-} \cdot 2\text{NH}_3$	(A)	1.013	-0.577 <sup>a</sup>	0.189 <sup>c</sup>	-0.740
	(B)	1.026	-0.583 <sup>b</sup>	0.142 <sup>d</sup>	-0.745
$[\text{PdCl}_4]^{2-} \cdot 3\text{NH}_3$	(A)	0.986	-0.571 <sup>a</sup>	0.186 <sup>c</sup>	-0.735
	(B)	0.999	-0.578 <sup>b</sup>	0.141 <sup>d</sup>	-0.737
$[\text{PdCl}_4]^{2-} \cdot 4\text{NH}_3$	(A)	0.977	-0.565 <sup>a</sup>	0.178 <sup>c</sup>	-0.726
	(B)	0.982	-0.570 <sup>b</sup>	0.140 <sup>d</sup>	-0.730
$[\text{PdCl}_4]^{2-} \cdot 5\text{NH}_3$	(A)	0.976	-0.552 <sup>a</sup>	0.173 <sup>c</sup>	-0.723
	(B)	0.981	-0.564 <sup>b</sup>	0.140 <sup>d</sup>	-0.728

<sup>a</sup>Atomic charges of P of  $\text{PH}_3$  and N of  $\text{NH}_3$  in the vertical direction.

<sup>b</sup>Atomic charges of P of  $\text{PH}_3$  and N of  $\text{NH}_3$  at the lower inclined plane.

<sup>c</sup>Atomic charges of the bridging H atom in the vertical interaction.

<sup>d</sup>Atomic charges of the H atom in the hydrogen bond of  $(\text{Cl} \cdots \text{H})$ .

pentamer,  $R_{(\text{Cl} \cdots \text{H})}$  and  $R_{(\text{Pd} \cdots \text{Cl})}$  increase and decrease, respectively. With increasing cluster size, the binding energies decrease stepwise. The planar  $\{[\text{PtCl}_4]^{2-} \cdot (\text{H}_2\text{O})_2\}$  complex with the hydrogen bond was optimized by Lienke *et al.*<sup>16</sup> The two H atoms of  $\text{H}_2\text{O}$  hydrogen bond to the two Cl atoms of  $[\text{PdCl}_4]^{2-}$ . In the previous experimental study of Caminiti *et al.*,<sup>4</sup> geometrical structures with apical  $(\text{M} \cdots \text{H}_2\text{O})$  interactions are observed. Our optimized structures are similar to the previously calculated<sup>1,16</sup> and experimental<sup>4</sup> results.

The average atomic charges of  $\{[\text{PdCl}_4]^{2-} \cdot n\text{PH}_3, (n = 1-5)\}$  and  $\{[\text{PdCl}_4]^{2-} \cdot n\text{NH}_3, (n = 1-5)\}$  are listed in Table 1. In the (A) type of  $\{[\text{PdCl}_4]^{2-} \cdot n\text{PH}_3, (n = 1-5)\}$ , the values of  $Q_{\text{Pd}}$ ,  $Q_{\text{H}}$ , and  $Q_{\text{Cl}}$  are more negative with increasing solvent size, while the values of  $Q_{\text{P}}$  are more positive. The atomic charges of Pd in the (A) type are more negative than those of Pd in the (B) type, while the atomic charges of P, the bridging H, and Cl are more positive than those of P, the bridging H, and Cl in the (B) type, respectively. In the (A) type with the direct  $(\text{Pd}^{\text{II}} \cdots \text{HPH}_2)$  interaction, charge transfer from  $\text{PH}_3$  to  $\text{Pd}^{\text{II}}$  occurs easier than those of the (B) type with the hydrogen bond of  $(\text{Cl} \cdots \text{HPH}_2)$ . The variations of the atomic charges from the soft  $\text{PH}_3$  solvent to the positively

charged  $\text{Pd}^{\text{II}}$  dication are in excellent agreement with the geometrical structures of  $[\text{PdCl}_4]^{2-} \cdot n\text{PH}_3$  with charge-dipole, dipole-dipole, and hydrogen bond interactions.

In conclusion, the outer sphere  $\{[\text{PdCl}_4]^{2-} \cdot \text{PH}_3\}$  complex of square pyramidal geometry is more stable than the inner sphere  $[\text{PdCl}_4(\text{PH}_3)]^{2-}$  complex of trigonal bipyramid by 0.18 eV. In  $\{[\text{PdCl}_4]^{2-} \cdot n\text{PH}_3, (n = 1-5)\}$ , the (A) types with a vertical  $(\text{Pd}^{\text{II}} \cdots \text{HPH}_2)$  interaction (charge-dipole) are more stable than the corresponding (B) types with both a  $(\text{Cl} \cdots \text{HPH}_2)$  hydrogen bond and a  $(\text{d}_{z^2} \cdots \text{HPH}_2)$  interaction (dipole-dipole). In  $\{[\text{PdCl}_4]^{2-} \cdot n\text{PH}_3$  and  $\{[\text{PdCl}_4]^{2-} \cdot n\text{NH}_3$ , with interactions of both the hydrogen bond and dipole-dipole type, the solvent is not located at the vertex of an octahedral symmetry, but is instead located at an inclined and marginal plane. In  $\{[\text{PdCl}_4]^{2-} \cdot n\text{H}_2\text{O}, (n = 1-5)\}$ , the geometrical structures with hydrogen bonds are the only ones optimized. In the solvated Pd complexes, charge transfer occurs from the solvent to the Pd(II) core via the charge-dipole of the vertical  $(\text{Pd}^{\text{II}} \cdots \text{solvent})$ , the hydrogen bond of  $(\text{Cl} \cdots \text{solvent})$ , and the dipole-dipole of  $(\text{d}_{z^2} \cdots \text{solvent})$ . With increasing cluster size, the binding energies decrease stepwise.

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